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### (54) Amine containing polymers and products therefrom

Aminoenthaltende Polymerisate und daraus geformte Produkte

Polymères contenant des groupes amino et produits en résultant

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**Description****TECHNICAL FIELD**

5 [0001] The subject invention relates to anionic polymerizations resulting in diene polymer and copolymer elastomers. More particularly, the present invention relates to polymerization employing a solubilized amine initiator. Specifically, the invention relates to a solubilized lithium amine initiator which is soluble in acyclic alkane solvents, and which will reproducibly polymerize monomers in a controllable and narrow molecular weight distribution range.

**10 BACKGROUND ART**

[0002] When conducting polymerizations on a commercial basis, it is important to utilize process conditions and components which will allow the molecular weight of the end products to be narrowly and reproducibly defined. The characteristics of a given polymer and its usefulness are dependent, among other things, upon its molecular weight.

15 Hence, it is desirable to be able to predict with some certainty the molecular weight of the end product of the polymerization. When the molecular weight is not narrowly definable, or is not reproducible on a systematic basis, the process is not commercially viable.

[0003] In the art, it is desirable to produce elastomeric compounds exhibiting reduced hysteresis characteristics. Such elastomers, when compounded to form articles such as tires, power belts and the like, will show an increase in 20 rebound, a decrease in rolling resistance and will have less heat build-up when mechanical stresses are applied.

[0004] A major source of hysteretic power loss has been established to be due to the section of the polymer chain from the last cross link of the vulcanize to the end of the polymer chain. This free end cannot be involved in an efficient elastically recoverable process, and as a result, any energy transmitted to this section of the cured sample is lost as heat. It is known in the art that this type of mechanism can be reduced by preparing higher molecular weight polymers 25 which will have fewer end groups. However, this procedure is not useful because processability of the rubber with compounding ingredients and during shaping operations decreases rapidly with increasing molecular weight.

[0005] It is difficult to obtain consistent properties, such as a reduction in hysteresis properties, if the polymer cannot be controllably reproduced in a narrow molecular weight range distribution. See, for example, U.S. Pat. No. 4,935,471, in which some polymers are prepared with a heterogeneous mixture of certain secondary amines, including lithium 30 pyrrolidide. Polymers made in this manner have widely variable molecular weights, broad polydispersities, and their functional terminations tend to reproduce erratically, giving rise to poorly reproducible hysteresis reduction results.

[0006] A major drawback with many of these known initiators, is that they are not soluble in acyclic alkanes, such as hexane. Polar solvents have heretofore been employed including the polar organic ethers such as dimethyl or diethyl ether, tetrahydrofuran, tetramethylethylenediamine, or diethylene glycol methyl ether (diglyme).

35 [0007] The present invention provides novel initiators for anionic polymerization, which are soluble in acyclic alkanes. The invention provides for the incorporation of a functionality from the initiator to be incorporated at the head and tail of the polymer chain. The invention provides for efficient, controllable and reproducible polymerizations, with the preparation of well defined end-products of a relatively narrow molecular weight range distribution.

**40 DISCLOSURE OF THE INVENTION**

[0008] It is therefore, an object of the present invention to provide an anionic polymerization initiator which is soluble in acyclic alkanes.

45 [0009] It is a further object of the present invention to provide a method of preparing such an anionic polymerization initiator.

[0010] It is still a further object of the invention to provide an initiator which will reproducibly result in a polymer within a narrow, predictable molecular weight range.

[0011] It is another object of the present invention to provide elastomers formed with such a polymerization initiator.

50 [0012] It is also an object of certain embodiments of the present invention to provide diene polymers and copolymers having reduced hysteresis characteristics.

[0013] It is a further object of the present invention to provide vulcanizable elastomeric compounds of diene polymers and copolymers having reduced hysteresis characteristics.

[0014] Still another object of the present invention is to provide an improved tire formed from an elastomer as described hereinabove.

55 [0015] At least one or more of these objects together with the advantages thereof over the existing art, which shall become apparent from the specification which follows, are accomplished by the invention as hereinafter described and claimed.

[0016] In general, according to the present invention, an anionic polymerization initiator which is soluble in acyclic

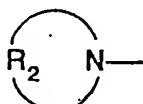
alkane solvents, comprises a solubilized lithio amine having the general formula



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where  $y$  is from about 1 to 3; SOL is a solubilizing component selected from the group consisting of hydrocarbons, ethers, amines or mixtures thereof; and, A is selected from the group consisting of cyclic amines having the general formula

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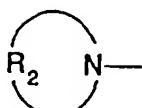
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where

$R_2$  is selected from the group consisting of a substituted alkylene group having from 8 to 16 methylene groups.

20 [0017] There is also provided a method of preparing an anionic polymerization initiator, which method comprises the steps of reacting an organolithium compound with a functionalizing agent in the presence of a solubilizing agent; the functionalizing agent being selected from the group consisting of cyclic amines having the general formula

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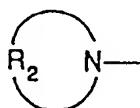


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where  $R_2$  is as defined hereinabove; and, the solubilizing agent is selected from the group consisting of hydrocarbons, ethers, amines or mixtures thereof.

35 [0018] A method of preparing an anionic polymerization initiator comprises the steps of reacting an organolithium compound with a functionalizing agent to form a reaction product. The functionalizing agent is selected from the group consisting of cyclic amines having the general formula

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where  $R_2$  is as defined hereinabove. The method also comprises the step of reacting the reaction product with a solubilizing agent selected from the group consisting of hydrocarbons, ethers, amines or mixtures thereof.

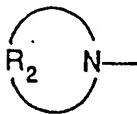
[0019] A functionalized polymer comprises a polymer chain carrying at least one functional group A wherein A is derived from a polymerization initiator having the general formula

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55 where  $y$  is of from about 1 to 3; SOL is a solubilizing component selected from the group consisting of hydrocarbons, ethers, amines or mixtures thereof; and, A is selected from the group consisting of cyclic amines having the general formula

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where  $R_2$  is as defined hereinabove.

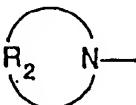
[0020] A method of forming a functionalized polymer, according to the invention, comprises the steps of forming a solution of one or more anionically polymerizable monomers in an alkane solvent; and, polymerizing the monomers in the presence of an initiator which is soluble in the alkane solvent. The initiator comprises a solubilized lithio amine having the general formula

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where  $y$  is from about 1 to 3;  $SOL$  is a solubilizing component selected from the group consisting of hydrocarbons, ethers, amines or mixtures thereof; and,  $A$  is selected from the group consisting of cyclic amines having the general formula

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where  $R_2$  is as defined hereinabove.

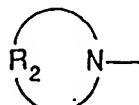
[0021] A vulcanizable elastomeric compound having reduced hysteresis properties comprises an elastomeric polymer having chains carrying at least one functional group  $A$ , wherein  $A$  is derived from a polymerization initiator having the general formula

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where  $y$  is of from about 1 to 3;  $SOL$  is a solubilizing component selected from the group consisting of hydrocarbons, ethers, amines or mixtures thereof; and,  $A$  is selected from the group consisting of cyclic amines having the general formula

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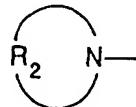
where  $R_2$  is as defined hereinabove; and from 5 to 80 parts by weight of carbon black, per 100 parts of the polymer.

[0022] The present invention also provides a tire having decreased rolling resistance resulting from a treadstock containing a vulcanizable elastomeric composition which comprises an elastomeric polymer having chains carrying at least one functional group  $A$  wherein  $A$  is derived from a polymerization initiator having the general formula



55 where  $y$  is of from about 1 to 3;  $SOL$  is a solubilizing component selected from the group consisting of hydrocarbons, ethers, amines or mixtures thereof; and,  $A$  is selected from the group consisting of cyclic amines having the general formula

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where  $R_2$  is as defined hereinabove; and from 5 to 80 parts by weight of carbon black, per 100 parts by weight of said polymer.

10 [0023] A vulcanizable rubber composition comprises a polymer carrying at least one amine functional group A, wherein A is derived from the reaction product of an organolithium compound and an amine; and a tin-carbon bond.

[0024] A multifunctional polymer comprises at least one functional group A, wherein A is derived from the reaction product of an organolithium compound and an amine; and, a tin-carbon bond.

15 [0025] A vulcanizable rubber composition comprises a polymer carrying at least one amine functional group A, wherein A is derived from the reaction product of an organolithium compound and an amine; and a second functional group selected and derived from the group consisting of terminating agents, coupling agents and linking agents.

[0026] A tire having at least one vulcanizable elastomeric component comprises a multifunctional polymer having at least one-functional group A, wherein A is derived from a polymerization initiator which is the reaction product of an organolithium compound and an amine, wherein the multifunctional polymer has a tin-carbon bond, and from 5 to 80

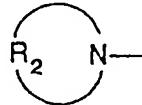
20 parts by weight of carbon black, per 100 parts of the polymer.

[0027] A multifunctional polymer comprises at least one functional group A, wherein A is derived from the reaction product of an organolithium compound and an amine; and a second functional group selected and derived from the group consisting of terminating agents, coupling agents and linking agents.

25 [0028] A tire having at least one vulcanizable elastomeric component is also provided, which component comprises a multifunctional polymer having at least one functional group A, wherein A is derived from a polymerization initiator which is the reaction product of an organolithium compound and an amine; the polymer having a second functional group selected and derived from the group consisting of terminating agents, coupling agents and linking agents; and from about 5 to 80 parts by weight of carbon black, per 100 parts of said polymer.

30 [0029] A functionalized polymer according to the invention comprises a polymer chain carrying at least one functional group selected from the group consisting of cyclic amine radicals having the general formula

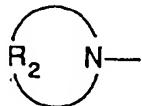
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where  $R_2$  is as defined hereinabove.

40 [0030] A functionalized polymer according to the invention also comprises a polymer chain having the general formula AYLi; wherein A is a functional group selected from the group consisting of cyclic amine radicals having the general formula

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where  $R_2$  is as defined hereinabove; and wherein Y is a divalent polymer radical selected from the group consisting of diene homopolymer radicals, monovinyl aromatic polymer radicals, diene/monovinyl aromatic random copolymer and block copolymer radicals.

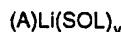
##### 55 PREFERRED EMBODIMENT FOR CARRYING OUT THE INVENTION

[0031] As will become apparent from the description which follows, the present invention provides novel polymerization initiators which are soluble in acyclic alkanes, including normal alkanes such as hexane, pentane, heptane,

isoheptane, octane, their alkylated derivatives, mixtures thereof, and the like. It has also been discovered herein that certain rubber compositions, vulcanizable elastomeric compositions and articles thereof based upon polymers formed using such initiators, exhibit useful properties, such as for example, reproducible relatively narrow molecular weight ranges. Furthermore, the polymers according to the invention also contain a functionality from the initiator, which functionality is useful for example, in reducing hysteresis properties.

[0032] While the initiators of the present invention are soluble in acyclic alkane solvents, it will be appreciated that the use of the initiators in other solvents is also within the scope of the invention.

[0033] The preferred initiator according to the invention, is the reaction product of an amine, an organo lithium and a solubilizing component. The organo lithium and the amine may be reacted in the presence of the solubilizing component or agent, or they may be reacted first and the reaction product thereof subsequently treated with the solubilizing component. The preferred initiator is therefore, a solubilized lithio amine having the general formula

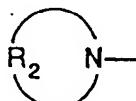


where  $y$  is from about 1 to 3. The parentheses of this general formula connote that the formula may include  $A-Li-SOL_y$ ;  $SOL_y-A-Li$ ; or,  $A-SOL_y-Li$ .

[0034] ( $SOL$ ) is a solubilizing component and may be a hydrocarbon, ether, amine or a mixture thereof. It has been discovered that by the presence of the ( $SOL$ ) component, the initiator is soluble in acyclic alkanes.

[0035] Exemplary ( $SOL$ ) groups include dienyl or vinyl aromatic polymers or copolymers having from 3 to about 300 polymerization units. Such polymers include polybutadiene, polystyrene, polyisoprene and copolymers thereof. Other examples of ( $SOL$ ) include polar ligands, such as tetrahydrofuran (THF) and tetramethylethylenediamine (TMEDA).

[0036] The ( $A$ ) component represents the amine functionality, at least one of which is carried by the resulting polymer, such as by being incorporated at the initiation site or head thereof. ( $A$ ) is a cyclic amine radical having the general formula



In this formula,

$R_2$  is a substituted alkylene group having from

8 to 16 methylene groups. The amino-alkylene group can be an N-alkylamino alkylene. By "substituted alkylene" it is understood that the alkylene has a substituent thereon. Preferred substituted alkynes include mono- to octa-substituted alkynes. The preferred substituents are linear or branched alkyls, cycloalkyls, bicycloalkyls, aryls and aralkyls having from 1 to 12 carbon atoms.

[0037] For example, ( $A$ ) may be derivative or radical of pyrrolidine; piperidine; monoalkyl-piperazine; perhydroazepine such as 3,3,5-trimethylhexahydroazepine; azacyclotridecane, also known as dodecamethyleneimine; azacycloheptadecane, also known as hexadecamethyleneimine; 1-azacycloheptadec-9-ene; or, 1-azacycloheptadec-8-ene; including bicyclics such as perhydroisoquinoline, perhydroindole, 1,3,3-trimethyl-6-azabicyclo [3.2.1] octane and the like.

[0038] Azacyclotridecane is preferred. A preferred pyrrolidine derivative is perhydroindole and a preferred piperidine is perhydroisoquinoline.

[0039] There are many useful examples of the alkyl, cycloalkyl, aryl and aralkyl substituents of the cyclic and bicyclic amines of the invention, including, but not limited to 2-(2-ethylhexyl)pyrrolidine; 3,5-bis(2-ethylhexyl) piperidine; 7-decyl-1-azacyclotridecane; 3,3-dimethyl-1-azacyclotetradecane; 4-dodecyl-1-azacyclooctane; 4-(2-phenylbutyl)-1-azacyclooctane; 3-ethyl-5-cyclohexyl-1-azacycloheptane; 4-hexyl-1-azacycloheptane; 9-isoamyl-1-azacycloheptadecane; 2-methyl-1-azacycloheptadec-9-ene; 3-isobutyl-1-azacyclododecane; 2-methyl-7-t-butyl-1-azacyclododecane; 5-nonyl-1-azacyclododecane; 8-(4'-methylphenyl)-5-pentyl-3-azabicyclo[5.4.0]undecane; 1-butyl-6-azabicyclo[3.2.1]octane; 8-ethyl-3-azabicyclo[3.2.1]octane; 1-propyl-3-azabicyclo[3.2.2]nonane; 3-(t-butyl)-7-azabicyclo[4.3.0]nonane; 1,5,5-trimethyl-3-azabicyclo[4.4.0]decane; and the like.

[0040] It has been found that when  $R_2$  is branched in the alkyl position, such as di-t-butyl, diisopropyl, tertiary butyl or the like, the resulting polymerizations are slow, presumably due to hinderance around the nitrogen at the initiation site. Hence, in a preferred embodiment of the invention, the carbon atoms in  $R_2$  which are bonded to the nitrogen in the amine, are also bonded to a total of at least three hydrogen atoms.

[0041] The initiator according to the present invention can be formed by preparing a solution of the amine component

(A), in an anhydrous, aprotic solvent, such as hexane, preferably in the presence of the solubilizing agent or component (SOL), if (SOL) is an ether or an amino compound. To this solution is then added an organolithium catalyst in the same or a similar solvent. The organolithium compound has the general formula RLi where R is selected from the group consisting of alkyls, cycloalkyls, alkenyls, aryls and aralkyls having from 1 to 20 carbon atoms and short chain length

5 low molecular weight polymers from diolefin and vinyl aryl monomers having up to about 25 units. Typical alkyls include n-butyl, s-butyl, methyl, ethyl, isopropyl and the like. The cycloalkyls include cyclohexyl, menthyl and the like. The alkenyls include allyl, vinyl and the like. The aryl and aralkyl groups include phenyl, benzyl, oligo(styryl) and the like. Exemplary short chain length polymers include the oligo(butadienyls), oligo(isoprenyls), oligo(styryls) and the like.

10 [0042] If (SOL) is a short chain length polymer, the monomers used to form (SOL) are added after the amine and the organolithium are mixed, as will be addressed hereinbelow. The initiator can also be formed by mixing the organolithium and the amine in the presence of the monomer.

15 [0043] To the solution of the amine and the organolithium, is added a solution of the monomers of the solubilizing component (SOL) in the same or similar solvent, if (SOL) is a polydiene or a polyvinyl aromatic. The three components are allowed to react for up to about one hour at ambient temperature (25° to 30° C), or elevated temperatures up to about 100°C preferably at less than 50°C, and more preferably at less than 38°C, following which the catalyst is ready for use. The initiators according to the present invention are considered to be soluble if they remain in solution within an excess of an acyclic alkane solvent for about 3 or more days.

20 [0044] As stated above, the initiator thus formed may be employed as an initiator to prepare any anionically-polymerized elastomer, e.g., polybutadiene, polyisoprene and the like, and copolymers thereof with monovinyl aromatics such as styrene, alpha methyl styrene and the like, or trienes such as myrcene. Thus, the elastomers include diene homopolymers and copolymers thereof with monovinyl aromatic polymers. Suitable monomers include conjugated dienes having from 4 to 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes. Examples of conjugated diene monomers and the like useful in the present invention include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene and 1,3-hexadiene, and aromatic vinyl monomers include styrene, alpha-methylstyrene, p-methylstyrene, vinyltoluene and vinylnaphthalene. The conjugated diene monomer and aromatic vinyl monomer are normally used at the weight ratios of 95-50:5-50, preferably 95-65:5-35.

25 [0045] Polymerization is conducted in an acyclic alkane solvent, such as the various hexanes, heptanes, octanes, mixtures thereof, and the like. In order to promote randomization in copolymerization and to control vinyl content, a polar coordinator may be added to the polymerization ingredients. Amounts range between 0 and 90 or more equivalents per equivalent of lithium. The amount depends on the amount of vinyl desired, the level of styrene employed and the temperature of the polymerization, as well as the nature of the specific polar coordinator (modifier) employed.

30 [0046] Compounds useful as polar coordinators are organic and include tetrahydrofuran (THF), linear and cyclic oligomeric oxolanyl alkanes such as 2-2'-di(tetrahydrofuryl) propane, di-piperidyl ethane, hexamethylphosphoramide, N-N'-dimethylpiperazine, diazabicyclooctane, dimethyl ether, diethyl ether, tributylamine and the like. The linear and 35 cyclic oligomeric oxolanyl alkane modifiers are described in U.S. Pat. No. 4,429,091. Compounds useful as polar coordinators include those having an oxygen or nitrogen hetero-atom and a non-bonded pair of electrons. Other examples include dialkyl ethers of mono and oligo alkylene glycols; "crown" ethers; tertiary amines such as tetramethylene diamine (TMEDA); linear THF oligomers and the like.

40 [0047] A batch polymerization is usually begun by charging a blend of monomer(s) and an acyclic alkane solvent to a suitable reaction vessel, followed by the addition of the polar coordinator (if employed) and the initiator compound previously described. The reactants are heated to a temperature of from 20 to 200°C, and the polymerization is allowed to proceed for from 0.1 to 24 hours. A functional amine group is derived from the initiator compound and attaches at the initiation site. Thus, substantially every resulting polymer chain, or the predominance of the chains, has the following general formula

45 AYLi

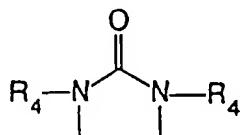
50 where A is as described above, and Y is a divalent polymer radical which is derived from any of the foregoing diene homopolymers, monovinyl aromatic polymers, diene/monovinyl aromatic random copolymers and block copolymers. The monomer addition at the lithium end causes the molecular weight of the polymer to increase as the polymerization continues.

55 [0048] To terminate the polymerization, and thus further control polymer molecular weight, a terminating agent, coupling agent or linking agent may be employed, all of these agents being collectively referred to herein as "terminating agents". Certain of these agents may provide the resulting polymer with a multifunctionality. That is, the polymers initiated according to the present invention, may carry at least one amine functional group A as discussed hereinabove, and may also carry a second functional group selected and derived from the group consisting of terminating agents, coupling agents and linking agents.

[0049] Useful terminating, coupling or linking agents include active hydrogen compounds such as water or alcohol; carbon dioxide; N,N,N',N'-tetradialkylamino-benzophenone (such as tetramethyldiaminobenzophenone or the like); N,N-dialkylamino-benzaldehyde (such as dimethylaminobenzaldehyde or the like); 1,3-dialkyl-2-imidazolidinones (such as 1,3-dimethyl-2-imidazolidinone or the like); 1-alkyl substituted pyrrolidinones; 1-aryl substituted pyrrolidinones; dialkyl- and dicycloalkyl-carbodiimides having from 5 to 20 carbon atoms;  $(R_3)_aZX_b$ ;

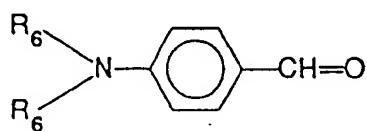
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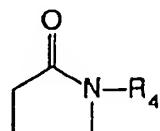
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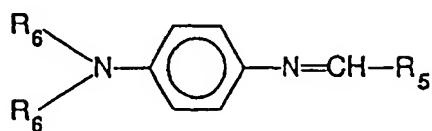


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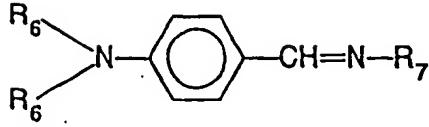


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40 and,

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50 where Z is tin or silicon. It is preferred that Z is tin.

[0050]  $R_3$  is an alkyl having from 1 to 20 carbon atoms; a cycloalkyl having from 3 to 20 carbon atoms; an aryl having from 6 to 20 carbon atoms; or, an aralkyl having from 7 to 20 carbon atoms. For example,  $R_3$  may include methyl, ethyl, n-butyl, neophyl, phenyl, cyclohexyl or the like.

[0051] X is chlorine or bromine, "a" is from 0 to 3, and "b" is from 1 to 4, where  $a + b = 4$ .

55 [0052] Each  $R_4$  is the same or different and is an alkyl, cycloalkyl or aryl, having from 1 to 12 carbon atoms. For example,  $R_4$  may include methyl, ethyl, nonyl, t-butyl, phenyl or the like.

[0053]  $R_5$  is an alkyl, phenyl, alkylphenyl or N,N-dialkylaminophenyl, having from 1 to 20 carbon atoms. For example,  $R_5$  may include t-butyl, 2-methyl-4-pentene-2-yl, phenyl, p-tolyl, p-butylphenyl, p-dodecylphenyl, p-diethylaminophenyl,

p-(pyrrolidino)phenyl, and the like.

[0054] Each R<sub>6</sub> is the same or different, and is an alkyl or cycloalkyl having from 1 to 12 carbon atoms. Two of the R<sub>6</sub> groups may together form a cyclic group. For example, R<sub>6</sub> may include methyl, ethyl, octyl, tetramethylene, pentamethylene, cyclohexyl or the like.

[0055] R<sub>7</sub> may include alkyls, phenyls, alkylphenyls or N,N-dialkylaminophenyls, having from 1 to 20 carbon atoms. For example, R<sub>7</sub> may include methyl, butyl, phenyl, p-butylphenyl, p-nonylphenyl, p-dimethylaminophenyl, p-diethylaminophenyl, p-(piperidino)phenyl, or the like.

[0056] Other examples of useful terminating agents include tin tetrachloride, (R<sub>1</sub>)<sub>3</sub>SnCl, (R<sub>1</sub>)<sub>2</sub>SnCl<sub>2</sub>, R<sub>1</sub>SnCl<sub>3</sub>, carbodiimides, N-methylpyrrolidinone, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino)benzophenone, and the like, where R<sub>1</sub> is as described hereinabove.

[0057] One preferred polymer according to the present invention, is a polymer which includes at least one functional group A as discussed hereinabove, wherein A is derived from the reaction product of an amine and an organolithium compound as also discussed hereinabove. Furthermore, a preferred polymer is multifunctional wherein the polymer also carries a tin-carbon bond, such as may be derived from the terminating, coupling or linking agent. A rubber composition or a vulcanizable rubber composition according to the present invention, may include such a polymer.

[0058] The terminating, coupling or linking agent is added to the reaction vessel, and the vessel is agitated for 1 to 1000 minutes. As a result, an elastomer is produced having an even greater affinity for compounding materials such as carbon black, and hence, even further reduced hysteresis. Additional examples of terminating agents include those found in U.S. Patent No. 4,616,069.

[0059] The polymer may be separated from the solvent by conventional techniques. These include steam or alcohol coagulation, thermal desolvantization, or any other suitable method. Additionally, solvent may be removed from the resulting polymer by drum drying, extruder drying, vacuum drying or the like.

[0060] The elastomers of the present invention comprise a plurality of polymers, having a functional group at both the head and tail of the resulting polymer. Such compounding may result in products exhibiting reduced hysteresis, which means a product having increased rebound, decreased rolling resistance and has less heat build-up when subjected to mechanical stress.

[0061] It has also been found, as will be exemplified hereinbelow, that polymers formed using the initiators of the invention, are reproducibly formable in a relatively narrow range of molecular weights, such that substantially consistently reproducible polymers are possible with a molecular weight range of 20,000 to 250,000.

[0062] The polymers of the present invention can be used alone or in combination with other elastomers to prepare a product such as a tire treadstock, sidewall stock or other tire component stock compound. Such stocks are useful for forming tire components such as treads, subtreads, black sidewalls, body ply skims, bead fillers and the like. At least one such component stock is produced from a vulcanizable elastomeric or rubber composition. For example, the polymers according to the invention can be blended with any conventionally employed treadstock rubber which includes natural rubber, synthetic rubber and blends thereof. Such rubbers are well known to those skilled in the art and include synthetic polyisoprene rubber, styrene/butadiene rubber (SBR), polybutadiene, butyl rubber, Neoprene, ethylene/propylene rubber, ethylene/propylene/diene rubber (EPDM), acrylonitrile/butadiene rubber (NBR), silicone rubber, the fluoroelastomers, ethylene acrylic rubber, ethylene vinyl acetate copolymer (EVA), epichlorohydrin rubbers, chlorinated polyethylene rubbers, chlorosulfonated polyethylene rubbers, hydrogenated nitrile rubber, tetrafluoroethylene/propylene rubber and the like. When the polymers of the present invention are blended with conventional rubbers, the amounts can vary widely such as between 10 and 99 percent by weight.

[0063] The polymers can be compounded with carbon black in amounts ranging from 5 to 100 parts by weight, per 100 parts of rubber (phr), with 5 to 80 parts being preferred and from 40 to 70 phr being more preferred. The carbon blacks may include any of the commonly available, commercially-produced carbon blacks but those having a surface area (EMSA) of at least 20 m<sup>2</sup>/g and more preferably at least 35 m<sup>2</sup>/g up to 200 m<sup>2</sup>/g or higher are preferred. Surface area values used in this application are those determined by ASTM test D-1765 using the cetyltrimethyl-ammonium bromide (CTAB) technique. Among the useful carbon blacks are-furnace black, channel blacks and lamp blacks. More specifically, examples of the carbon blacks include super abrasion furnace (SAF) blacks, high abrasion furnace (HAF) blacks, fast extrusion furnace (FEF) blacks, fine furnace (FF) blacks, intermediate super abrasion furnace (ISAF) blacks, semi-reinforcing furnace (SRF) blacks, medium processing channel blacks, hard processing channel blacks and conducting channel blacks. Other carbon blacks which may be utilized include acetylene blacks. Mixtures of two or more of the above blacks can be used in preparing the carbon black products of the invention. Typical values for surface areas of usable carbon blacks are summarized in the following TABLE I.

TABLE I

CARBON BLACKS	
ASTM Designation (D-1765-82a)	Surface Area (m <sup>2</sup> /g) (D-3765)
N-110	126
N-220	111
N-339	95
N-330	83
N-550	42
N-660	35

[0064] The carbon blacks utilized in the preparation of the rubber compounds of the invention may be in pelletized form or an unpelletized flocculent mass. Preferably, for more uniform mixing, unpelletized carbon black is preferred. The reinforced rubber compounds can be cured in a conventional manner with known vulcanizing agents at about 0.5 to about 4 phr. For example, sulfur or peroxide-based curing systems may be employed. For a general disclosure of suitable vulcanizing agents one can refer to Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., Wiley Interscience, N.Y. 1982, Vol. 20, pp. 365-468, particularly "Vulcanization Agents and Auxiliary Materials" pp. 390-402. Vulcanizing agents may be used alone or in combination.

[0065] Vulcanizable elastomeric or rubber compositions of the invention can be prepared by compounding or mixing the polymers thereof with carbon black and other conventional rubber additives such as fillers, plasticizers, antioxidants, curing agents and the like, using standard rubber mixing equipment and procedures and conventional amounts of such additives.

## GENERAL EXPERIMENTAL

[0066] In order to demonstrate the preparation and properties of the initiators and elastomers according to the present invention, a number of such initiators and elastomers were prepared. A solution of styrene and butadiene monomers in hexane was prepared and was polymerized with the above described initiators. To further show the effectiveness of the invention, a number of similar monomer solutions were polymerized with a heterogenous mixture of non-solubilized lithium pyrrolidide as an initiator to provide comparative control examples. The non-solubilized lithium pyrrolidides will be discussed first hereinbelow, followed by examples of initiators and elastomers made according to the present invention. As noted above, various techniques known in the art for carrying out polymerizations may be employed without departing from the scope of the present invention.

### I. Non-Solubilized Lithium Pyrrolidide Initiation

[0067] The following examples are included for comparison to the initiators and elastomers prepared according to the invention, which will be exemplified hereinbelow.

#### Experiment No. 1

##### Initiator Preparation

[0068] In a small dried and nitrogen purged bottle, 20 ml of a 0.5 M solution of pyrrolidine in hexanes (10 milliequivalent or "meq") was treated with 6.36 ml of a 1.65 M solution of n-butyllithium in hexanes (10.5 meq). The bottle was fitted with a perforated crown seal having a rubber liner. The resulting heterogeneous mixture was agitated gently at room temperature for 16 hours, after which the product was drawn off for use as an initiator. The mixture was shaken vigorously before and while drawing off the samples.

##### Polymerization

[0069] The initiator mixture made in the above manner was transferred by syringe to each of two small bottles which were also fitted with a seal as above. The bottles each contained a 75/25 weight percent monomer blend of butadiene/styrene, at 25 weight percent in hexane and a level of 1.0 meq Li/100 grams of monomer. The bottles also contained 0.6 mol of N,N,N',N'-tetramethylethylenediamine (TMEDA) per mol of lithium. The mixtures were agitated at 50° C for 2.5 hours. The reaction resulted in approximately 100 percent conversion of monomer to polymer.

[0070] The first bottle of cement, EXAMPLE 1, was then quenched by injection of 1.5 milliliters (ml) of isopropyl alcohol (i-PrOH), and the second bottle of cement, EXAMPLE 2, was treated for an additional 90 minutes at 50° C with 1.15 mol of 4-(N,N-diethylamino) benzaldehyde per mol of lithium. The cement of EXAMPLE 2 was then quenched with 1.5 ml of i-PrOH.

[0071] Both cements from EXAMPLE 1 and EXAMPLE 2 were treated with an antioxidant, namely, 2 ml of a mixture containing 2.0 weight percent of dibutyl paracresol (DBPC) and 0.7 weight percent of UOP-88, available from Universal Oil Products Co., in hexane. The cements were then coagulated in i-PrOH and drum dried. The resulting polymers were analyzed, and the characteristics thereof are reported in TABLE II hereinbelow.

TABLE II

ANALYSIS OF POLYMERS FROM EXAMPLES 1 AND 2		
HNMR	Example 1 24% styrene (0% block styrene)	Example 2 24.8% styrene (0% block styrene)
Percent of butadiene portion as 1,2 linkages	51.9%	49.4%
GPC (THF solvent)		
Mn	136365	136697
Mw/Mn	1.35	1.40
Tg <sup>a</sup>	-36.5°C	-38.8°C

a) glass transition temperature at onset

[0072] The polymers of EXAMPLES 1 and 2 were compounded using the rubber recipe reported in TABLE III hereinbelow.

TABLE III

COMPOUNDING RECIPE			
Ingredient	Mix Order	Parts per Hundred Parts Rubber	
Polymer	1	100	
Naphthenic oil	2	10	
Carbon black, N-351	3	55	Masterbatch 145-155°C, 60 RPM
ZnO	4	3	
Antioxidant	5	1	
Wax blend	6	2	
	Total Masterbatch:	171	
Stearic acid		2	Final
Sulfur		1.5	77-93°C, 40 RPM
Accelerator		1	
	Total Final:	175.5	

[0073] The compounded polymers were then cured using 3.8 x 10.2 x 0.1cm (1.5 inch x 4 inch x 0.040 inch) tensile plaques, for 45 minutes at 149°C (300°F); Dynastat buttons, 50 minutes at 149°C (300°F). The results of ensuing physical tests are reported in TABLE IV.

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TABLE IV  
PHYSICAL TESTS OF COMPOUNDED POLYMERS OF EXAMPLES 1 AND 2

Example No.	MLU4/212 (gum) (cpd)	Wt% Bound Rubber	1 Hz Dynastat tan $\delta$ 50°C	Ring Stress-Stain, MPa(psi), RT		
				M300	T.S.	%EB
1	32	81	28	0.110	14.96 (2169)	2.89(419)
2	33	84	ca.29	0.107	15.01 (2177)	2.48(359)

[0074] The test results reported in TABLE IV, show that the compounded polymer of EXAMPLE 1 has a tan  $\delta$  value about 30 percent below the value expected for an unmodified polymer of this molecular weight, prepared using a typical alkylolithium initiator. However, the polymer of EXAMPLE 2 fails to show any significant reduction in tan  $\delta$  beyond this, despite its having been additionally treated at the tail with a reagent which is known to be effective for reducing tan  $\delta$ . The lack of additional effect was also noted in the bound rubber results, where the result for EXAMPLE 2 was not

significantly different from that of EXAMPLE 1.

[0075] It was concluded that the polymer cement prepared in this manner, besides having somewhat broadened molecular weight distribution, also did not have sufficient live C-Li chain ends after polymerization to allow for significant reaction with a chain-end functionalizing reagent. Therefore, this method was not highly desirable for synthesis of polymers with optimum properties.

### Experiment No. 2

#### Initiator Preparation

[0076] A second non-solubilized Initiator was prepared. In a clean, stirred, 3.8 l (one gallon) stainless steel reactor, which had been dried and preconditioned, and then nitrogen purged, was placed 554g (1.22 pounds) of anhydrous hexanes, and 5.4 ml of a 0.77 M solution of pyrrolidine in hexanes (4.16 meq). This was treated with 2.69 ml of a 1.58 M solution of n-butyllithium in hexanes (4.25 meq), stirring at room temperature overnight. The resulting heterogeneous mixture was used in situ for the subsequent polymerization.

#### Polymerization

[0077] The reactor containing the above initiator mixture was charged with 345g (0.76 pounds) of a 34 weight percent blend of styrene and hexanes, 1.28 mmol of TMEDA, and 1.4kg (3.06 pounds) of a 25.5 weight percent blend of 1,3-butadiene in hexanes. The reactor was heated to 46°C and controlled at that temperature for three hours.

[0078] A portion of the polymer cement made in this manner was transferred by needle into three small bottles sealed as in Experiment 1 hereinabove. The remainder of the cement was collected in a large glass container, under a nitrogen purge. The cement in the large container, EXAMPLE 3 was quenched by injection with 1.5 ml of isopropyl alcohol (i-PrOH), while the cement in the small bottles, EXAMPLE 4 was treated for an additional 2 hours at 50°C with 1.25 mol of 1,3-dimethylimidazolidin-2-one (1,3-DMI) per mol of lithium. The cement of EXAMPLE 4 was then quenched with 1.5 ml of i-PrOH, and both cement portions were treated with an antioxidant (2 ml of a mixture containing 2.0 wt. percent DBPC in hexane). The contents of the bottles were combined, and both EXAMPLES 3 and 4 were coagulated separately in i-PrOH and drum dried. Suitable characterizations were performed, and the results are summarized in TABLE V hereinbelow.

### Experiment No. 3

[0079] Repeat experiments were run using the same reactor as in Experiment No. 2, employing the same amount of reagents, reaction times, and temperatures from those of EXAMPLES 3 and 4. The resulting cement was compounded in the recipe of TABLE III hereinabove, and is reported as EXAMPLE 5 hereinbelow. A portion of EXAMPLE 5 was end-linked by reaction with one equivalent of  $\text{SnCl}_4$  per equivalent of lithium, to produce EXAMPLE 6. A cement was also prepared as for EXAMPLE 5, except that the initiator was allowed to form in the reactor for three (3) days instead of overnight. Also, the resulting polymer was compounded in the recipe of TABLE VI hereinabove, and is reported herein as EXAMPLE 7. A portion of EXAMPLE 7 was treated with 1.25 mole of 4-(N,N-dimethylamino)-benzylidene butylaniline per mole of lithium to produce EXAMPLE 8. The order of addition of polymerization reagents for the run producing EXAMPLE 7 and 8 were as follows: (1) TMEDA, (2) butadiene blend, (3) styrene blend. The polymeric products were worked up as described for EXAMPLES 3 and 4. Results of their characterization and compounded evaluation are given in TABLE V hereinbelow.

[0080] The product polymers were cured using 3.8 x 10.2 x 0.1cm (1.5 inch x 4 inch x 0.040) tensile plaques for 20 minutes at 165°C; and Dynastat buttons, for 25 minutes and 165°C. TABLE V hereinbelow lists the characterizations and compounded properties of Examples 5 to 8.

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TABLE V  
SUMMARY OF CHARACTERIZATION AND COMPOUNDED PHYSICAL PROPERTIES  
OF EXAMPLES 3-8

Example No.	5		6		3		4		7		8		3,4,7,8 Control <sup>a</sup>	
	NMR % VINYL b													
NMR % STY	52.9	52.9			70.0	70.0			63.6	63.6			ca.40	
DSC T <sub>g</sub> , °C <sup>c</sup>	22.4	22.4	22.0	22.0			22.0	22.0	26.6	26.6			ca.20	
GPC (THF)	-42	-42	-24	-24			-24	-24	-24	-24			ca.40	
M <sub>n</sub> x 10 <sup>-3</sup>	95.8	221	254	228			201	201	197	197			ca.200	
M <sub>w</sub> /M <sub>n</sub>	1.1	2.2	2.5	2.3			1.4	1.4	1.2	1.2			ca.2.4	
Coupling	-	78%	-	-			-	-	-	-			-	
M <sub>1</sub> /4/100 °C														
Raw	8	67	108	109			77	77	72	72			ca.140	
Compound	34	71	94	101			72	72	75	75			74	
Test Recipe,														
TABLE NO.	III	III	VI	VI			VI	VI	VI	VI			VI	
STRESS M300 <sup>d</sup>	14.6(2116)19.2(2780)	9.3(1361)10.7(1547)10.5(1520)10.7(1556)											8.8(1276)	
-STRAIN, T <sub>B</sub> <sup>e</sup>	21.5(3115)18.8(2728)	16.4(2373)18.4(2667)8.3(2649)18.1(2631)											2.4(3551)	
23 °C % EB <sup>f</sup>	455	344	503	497			507	507	491	491			653	

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TABLE V (Continued)

% BOUND RUBBER <sup>a</sup>	21	37	34	40	27	37	32
DYNASTAT 1 HZ, tan δ 50°C	0.144	0.078	0.156	0.138	0.162	0.143	0.186
	0.167	0.109	0.180	0.219	0.231	0.219	0.227

a) Blend of unmodified SBR's run in comparison with EXAMPLES 3, 4, 7, 8 in formulation of TABLE VI  
 b) Mol% of butadiene content as 1,2-linkages  
 c) Onset of T<sub>g</sub>  
 d) Average ring stress-strain, 300% modulus,(psi) MPa  
 e) Average ring stress-strain, tensile modulus,(psi) MPa  
 f) Average percent elongation at break  
 g) Weight percentage of rubber content in C-black filled compound found insoluble in toluene after 2 days at room temperature, with no agitation

TABLE VI  
MEDIUM-OIL COMPOUNDING FORMULATION

5	Ingredient	Mix Order	Parts per Hundred Parts Rubber	
			100	
10	Polymer	1	100	
	Carbon black	2	54	Masterbatch
	ZnO	3	3	145° - 185°C 60 RPM
15	Stearic acid	4	2	
	Antioxidant/Processing aids	5	4.25	
	Aromatic oil	6	<u>27.6</u>	
	Total Masterbatch:		<u>190.85</u>	
20				
	Sulfur		2.25	Final 77° - 93°C 40 RPM
	Accelerator blend		<u>2.15</u>	
25	Total Final:		<u>195.25</u>	

[0081] The results in TABLE V show the shortcomings of polymerization with N-lithiopyrrolidide initiators. Although the initiator/monomers charged in runs 3,5 and 7 were the same (1.0 meq of lithium per 100 grams of monomer), the molecular weight of the products ranged from 96,000 to 254,000, which is evidence of the highly erratic initiator. The high molecular weight products are indicative of slow initiation relative to propagation, presumably due to the heterogeneous nature of the system. EXAMPLE 5 exhibited a tan δ reduction at 50°C about 31% lower than that of an unmodified polymer of similar microstructure and molecular weight. The result of end-linking of the live cement of EXAMPLE 5, via  $\text{SnCl}_4$ , leading to EXAMPLE 6 was a further reduction in tan δ, to about 40% of that of an unmodified polymer of the same base (uncoupled) molecular weight. The bound rubber content, which is indicative of the extent of interaction with carbon black, increased appreciably while the GPC showed that 78 percent of the polymer chains were end-linked, an indication that an appreciable fraction of "live" chain-ends were still available for linking.

[0082] EXAMPLES 3, 4 and 7, 8 resulted in polymers of such high molecular weight that they were not processable for formulation in the low oil recipe of TABLE III, but were formulated according to the recipe of TABLE VI, which contains 27 parts per 100 rubber of oil for better processing. The results of the evaluations in TABLE V indicate that these polymers show reduced tan δ, but the 13-16 percent reduction relative to the unmodified SBR elastomers is small compared to that demonstrated in the EXAMPLES 5 and 6. Little change in viscosity occurred upon attempting end-linking with  $\text{SnCl}_4$ , indicating that there was little active C-Li remaining at the chain ends after polymerization in these polymers. The  $\text{SnCl}_4$ -treated polymers (EXAMPLES 4 and 8) exhibited tan δ's which were about 75 percent of that of the unmodified samples.

[0083] In summary, the results of polymerizations which were initiated using N-lithiopyrrolidide as described hereinabove, were highly erratic, both with respect to the nature and composition of the product as well as to other characteristics thereof.

## II. Polymerization with a Solubilized Initiator (Examples included for reference) Experiment No. 4

### 50 Initiator Preparation

[0084] A dried, stainless steel 3.8 l (one gallon) reactor under a nitrogen atmosphere, was charged with 554g (1.22 pounds) of hexane, and then with 5.4 ml of 0.77 M pyrrolidine in hexane (4.16 meq) followed by 2.7 ml of 1.58 M n-butyllithium in hexane (4.27 meq). The mixture was stirred overnight at 32°C (90°F). The reactor was then charged with 90 grams of 25.4 weight percent 1,3-butadiene in a hexane solution (423 mmol of butadiene), and the mixture was heated at 43 to 49°C (110 to 120°F) for one hour. This effectively places a SOL group on the pyrrolidine moiety consisting on average of about 100 parts of 1,3-butadiene.

**Polymerization**

[0085] There was then charged to the reactor, 345g (0.76 pounds) of 33 weight percent styrene in hexane, containing 1.06 mmol of TMEDA, followed immediately by 1312g (2.89 pounds) of the 25.4 weight percent butadiene/hexane blend. This provided for an initiator to monomer charged ratio of 1.0 meq of lithium per 100 grams of monomer (1.0 meq Li/phgm). The polymerization was allowed to continue for 2 hours at 49°C (120°F) and the live cement was collected through a twelve gauge stainless steel needle into four small beverage bottles, fitted and purged as described in the preceding examples.

[0086] The cements in two of the bottles, EXAMPLE 9, were quenched by injection with 1.5 ml of i-PrOH, while the cements in the other two bottles, EXAMPLE 10, were treated for an additional two hours at 50°C with 1.2 mol of tributyltin chloride per mol of lithium. The cement of EXAMPLE 10 was then quenched with 1.5 ml of i-PrOH, and both cement portions were treated with an anti-oxidant as in Experiment III hereinabove. Both EXAMPLES 9 and 10 were coagulated separately in i-PrOH and drum dried. Suitable characterizations were performed, and the results are summarized in TABLE VII hereinbelow.

**Experiment No. 5****Initiator Preparation**

[0087] A mixture of 25.1 meq of pyrrolidine and 25.1 meq of n-butyllithium in hexane was stirred under nitrogen over a weekend at room temperature. This was treated with 50.2 meq of THF in hexane, and the resulting mixture was used to initiate the polymerization.

**Polymerization**

[0088] A dried, stainless steel 18.5l (five gallon) reactor under a nitrogen atmosphere, was charged with 3.87kg (8.53 pounds) of hexane, 1.44kg (3.17 pounds) of 33 weight percent styrene in hexane, 8.78 mmol of TMEDA, followed immediately by 8.12kg (17.89 pounds) of a 25.4 weight percent butadiene/hexane blend, and the initiator prepared hereinabove, contained 25.1 meq of lithium. The polymerization was run for 2.25 hours at 43 to 49°C (110 to 120°F) and the live cement was collected through a twelve gauge stainless steel needle into five small beverage bottles, fitted and purged as described in the previous examples, and through a 1.3cm (1/2 inch) pipe into two dried and purged large containers under a nitrogen purge.

[0089] The cements in the large containers, EXAMPLE 11, were quenched by injection with i-PrOH, while the cements in the bottles, EXAMPLE 12, were treated first for an additional 0.5 hours at 50°C with 0.3 equivalents of tin tetrachloride per mol of lithium, followed by treatment for 2 hours at 50°C with 0.84 mols of 1,3-dimethyl-2-imidazolidinone (1,3-DMI) per mol of lithium. The cement remaining in the reactor, EXAMPLE 13, was treated for about 2 hours at 50°C with 0.8 equivalents of  $\text{SnCl}_4$  per equivalent of lithium. The polymeric products were worked up as described for EXAMPLES 9 and 10 hereinabove. Results of their characterizations and compounded evaluations are given in TABLE VII hereinbelow.

**Experiment No. 6****Initiator Preparation**

[0090] A separate portion of the same initiator used in EXAMPLES 11, 12 and 13 was set aside and used two days later as follows, with an estimated concentration of 0.6 meq/ml.

**Polymerization**

[0091] The procedure used to polymerize the base cement of EXAMPLES 11-13 was repeated. The live product cement was collected through a twelve gauge stainless steel needle into five small beverage bottles, fitted and purged as described in the preceding examples and through a 1.3 cm (1/2 inch) pipe into two dried and purged large containers under a nitrogen purge.

[0092] The cements in the large containers in EXAMPLE 14, were quenched by injection with i-PrOH while the cements in the bottle, EXAMPLE 15, were treated first for an additional 0.5 hours at 50°C with 0.3 equivalents of tin tetrachloride per mol of lithium, followed by treatment for 2 hours at 50°C with 0.85 mol of 1,3-DMI per mol of lithium. The polymeric products were worked up as described for EXAMPLES 9 and 10, results of their characterizations and compounded evaluations are given in TABLE VII hereinbelow.

TABLE VII  
SUMMARY OF CHARACTERIZATION AND COMPOUNDED PHYSICAL PROPERTIES  
OF EXAMPLES 9-15

EXAMPLE NO.	9	10	11	12	13	14	15
NMR % VINYL <sup>b</sup>	42.7	42.7	53.3	53.3	53.3	50.1	50.1
% STY	19.4	19.4	20.6	20.6	20.6	20.6	20.6
DSC T <sub>g</sub> , °C <sup>c</sup>	-45	-45	-38	-38	-38	-43	-43
GPC (THF)							
M <sub>n</sub> x 10 <sup>-5</sup>	1.45	1.44	1.30	2.42	2.45	1.13	2.09
M <sub>w</sub> /M <sub>n</sub>	1.15	1.17	1.14	1.79	2.09	1.15	1.94
Coupling	-	-	-	53%	64%	-	54%
ML4/100°C							
Raw	24	24	29	78	94	19	76
Compound	70	90	82	103	114	76	107
Test Recipe,							
TABLE NO.	III						
STRESS-STRAIN M300 <sup>c</sup>	14.7 (2125)	17.3 (2514)	15.0 (2177)	16.4 (2374)	20.0 (2903)	20.0 (2903)	18.7 (2706)
STRESS-STRAIN, T <sub>B</sub> <sup>d</sup>	19.5 (2832)	22.6 (3275)	20.6 (2982)	20.4 (2956)	23.8 (3445)	23.5 (3418)	23.8 (3451)
23°C % EB <sup>e</sup>	419	409	431	403	387	395	409

TABLE VII (Continued)

% BOUND RUBBER <sup>f</sup>	28.4	49.5	31.3	42.0	42.3	-g	-g
DYNASTAT 1 HZ, tan $\delta$ +50°C	0.079	0.056	0.080	0.076	0.078	0.129	0.103
tan $\delta$ -20°C	0.374	0.389	0.675	0.684	0.431	0.541	0.563

a) Mol% of butadiene content as 1,2-linkages  
 b) Onset of  $T_g$   
 c) Average ring stress-strain, 300% modulus,(psi) MPa  
 d) Average ring stress-strain, tensile modulus,(psi) MPa  
 e) Average percent elongation at break  
 f) Weight percentage of rubber content in C-black filled compound found insoluble in toluene after 2 days at room temperature, with no agitation  
 g) Not tested

## Experiment No. 7

## Initiator Preparation

5 [0093] A mixture of 28.6 meq of pyrrolidine, 57.2 mmol of THF, and 29.15 meq of n-butyllithium in hexane, was stirred under a nitrogen atmosphere overnight at room temperature. An aliquot from the resulting mixture (about 0.56 milliequivalent (meq) per ml) was used to initiate the polymerization.

10 [0094] A 18.5 l (five gallon) stainless steel reactor was then charged with 2.91kg (6.42 pounds) of hexane, 28.6 mol equivalent of the above 0.56 M initiator, and 0.545kg (1.25 pounds) of a 24.2 weight percent blend of butadiene and hexane, and the mixture was heated at 35°C (100°F) for one hour.

## Polymerization

15 [0095] There was then charged to the reactor, 1.60kg (3.53 pounds) of 34 weight percent styrene in hexane, 9.7 mmol of TMEDA, and 8.10kg (17.85 pounds) of the butadiene/hexane blend. This provided for an initiator to monomer charge ratio of 1.05 meq Li phgm, and a monomer ratio of approximately 20 weight percent styrene/80 weight percent butadiene. The polymerization was run for 1.75 hours at 43 to 46°C (110 to 115°F). The reactor was finally charged with 136g (0.3 pounds) of the butadiene/hexane blend, and a 1.86kg (4.1 pound) sample of the cement was immediately collected in a large container and quenched by adding i-PrOH, EXAMPLE 16. The contents remaining in the reactor were treated by stirring with 22.2 ml of 1.0 N  $\text{SnCl}_4$  for 1.5 hours at 43 to 46°C (100 to 110°F) and the cement was dropped under a nitrogen purge into a 19l (five gallon) canister containing a small amount of i-PrOH EXAMPLE 17.

20 [0096] The cements from EXAMPLES 16 and 17 were treated with an antioxidant as in the immediately preceding experiment, and both samples were coagulated in i-PrOH and drum dried. Suitable characterizations were performed and the results are summarized in TABLE VIII hereinbelow.

## Experiment No. 8

## Initiator Preparation

30 [0097] A mixture of 88.8 meq of pyrrolidine, 177.8 mmol of THF, and 89.8 meq of n-butyllithium in hexane was stirred under nitrogen overnight at room temperature. An aliquot from the resulting mixture (approximately 0.57 meq per ml) was used to initiate polymerization.

35 [0098] A 19l (five gallon) stainless steel reactor was then charged with 3.0kg (6.55 pounds) of hexane, 47.1 ml (26.7 meq) of the above 0.57 M initiator, and 454g (1.0 pound) of a 24.2 weight percent blend of butadiene in hexane, and the mixture was heated at 38°C (100°F) for 30 minutes.

## Polymerization

40 [0099] There was then charged into the reactor, 2.00kg (4.41 pounds) of 34 weight percent styrene in hexane, 9.08 mmol of TMEDA, and 7.7kg (17.1 pounds) of the butadiene/hexane blend. This provided for an initiator to monomer charge ratio of 0.98 meq Li phgm, and a monomer ratio of approximately 25 weight percent styrene/75 weight percent butadiene. The polymerization was run 2.3 hours at 43 to 46°C (110 to 115°F). The reactor was finally charged with 227g (0.5 pounds) of the butadiene/hexane blend, and a 1.6kg (3.5 pound) sample of the cement was immediately collected in a large container and quenched by adding i-PrOH, EXAMPLE 18. The contents remaining in the reactor were treated by stirring with 21.0 ml of 1.0 N  $\text{SnCl}_4$  at 46°C (115°F). After reaction, the cement was dropped under a nitrogen purge into a five gallon canister containing a small amount of i-PrOH, EXAMPLE 19. The cements were treated with an antioxidant as in the immediately preceding example and both cements from EXAMPLES 18 and 19 were coagulated separately in i-PrOH and then drum dried. Suitable characterizations were performed and the results are summarized in TABLE VIII hereinbelow.

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TABLE VIII

SUMMARY OF CHARACTERIZATION AND COMPOUNDED PHYSICAL PROPERTIES OF EXAMPLES 16-19					
Example No.		16	17	18	19
5	NMR	% VINYL <sup>b</sup>	42.7	43.1	43.4
		% STY	20.4	20.1	24.9
	DSC $T_g$ , °C <sup>c</sup>		-47	-46	-45
10	GPC (THF)				
	$M_n \times 10^{-5}$		1.00	2.41	1.22
	$M_w/M_n$		1.10	1.48	1.26
	Coupling		-	86%	-
15	ML/4/100°C				
	Raw		7	82	20
	Compound		47	94	61
	Test Recipe, TABLE NO.		III	III	III
20	STRESS-STRAIN M300 <sup>c</sup>		14.9 (2165)	17.4 (2525)	18.2 (2643)
	STRESS-STRAIN,TB <sup>d</sup>		21.8 (3167)	23.8 (3452)	22.6 (3283)
	23°C % EB <sup>e</sup>		447	423	405
	DYNASTAT 1 HZ,				
25	$\tan \delta +50^\circ\text{C}$		0.100	0.079	0.098
	$\tan \delta -20^\circ\text{C}$		0.289	0.312	0.495
30	a) Mol% of butadiene content as 1,2-linkages				
	b) Onset of $T_g$				
	c) Ring stress-strain, 300% modulus, (psi) MPA				
	d) Ring stress-strain, tensile modulus, (psi) MPA				
	e) % Elongation at break				

[0100] The product polymers were compounded and tested as indicated in the test recipes show in TABLE III, and cured as above. TABLE VII lists the characterizations and properties of the polymers from EXAMPLES 9-15. TABLE VIII lists the characterizations and compounded properties of EXAMPLES 16-19.

[0101] The results in TABLES VII and VIII show the advantages and the desirable results obtained from polymerization with the initiators according to the present invention. In contrast to the results in TABLE V, EXAMPLES 9-19 demonstrate the consistency of diene polymerizations employing these Initiators. Namely, the polymerizations show relatively reproducible and predictable molecular weights, with narrow molecular weight distributions, and the polymer cements exhibit better viability of the living C-Li chains for further reactions. The dicapped polymers of EXAMPLES 10, 12, 13 and 17 show exceptionally low hysteresis, at about 40 percent to 50 percent of the values expected for comparable unmodified polymers of the same base molecular weight.

[0102] EXAMPLES 6, 10, 12, 13, 17 and 19 also exhibit the advantageous combination of N-Li Initiation and end-linking or termination with a tin compound, such as  $R_3SnCl$  or  $SnCl_4$ .

[0103] The results of polymerizations which were Initiated in acyclic alkane solvents using the lithium pyrrolidide as described in the comparative EXAMPLES 1-8, were highly erratic both with respect to the nature and composition of the products as well as their hysteresis behavior. However, when formulated as the N-lithiohydrocarbon amide with near-equivalent amounts of polar ligand or with monomer extension, as exemplified hereinabove, reproducible polymerizations with good molecular weight control, narrow molecular weight distributions, and good preservation of living C-Li ends for further reactions are achieved.

## Experiment No. 9

PREPARATION OF POLYMER FROM  $C_{12}H_{24}NLi\cdot2THF$  INITIATOR5 Preparation of  $C_{12}H_{24}NLi\cdot2THF$  Initiator:

[0104] Dodecamethylenelmine ("DDMI") was vacuum distilled from calcium hydride and transferred under nitrogen to a dried, nitrogen-purged bottle. The N-lithio salt of DDMI was prepared by treating 10 ml of a 0.4 M solution of DDMI in hexanes with 2 ml of a 4.0 M solution of THF in hexanes, followed by the slow addition of 2.35 ml of a 1.7M solution of n-butyllithium in hexanes, with gentle swirling. Swirling was continued at room temperature overnight. The resulting 0.28M solution was a clear, pale yellow. If the DDMI were treated by rapid addition of n-butyllithium, or in the absence of at least about 2 equivalents of the THF, cloudiness and/or precipitation occurred right away. The  $C_{12}H_{24}NLi\cdot2THF$  solution was stable for at least several days at room temperature. Samples were drawn from it by syringe for use in initiating polymerization.

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Polymerization of Butadiene and Styrene with  $C_{12}H_{24}NLi\cdot2THF$  or n-BuLi:

[0105] A 0.28 M solution of the above initiator was added to sealed bottles containing an 80%/20% by weight blend of butadiene and styrene in hexanes, at a level of 1.0 meq Li/100 grams monomer, and N,N,N',N'-tetramethylethylenediamine ("TMEDA") was added at 0.45 TMEDA/Li (mol/mol). The mixtures were agitated at 50°C for 2.5 hr, proceeding to approximately 90-100% conversion to polymer. In practice, there is considerable leeway in the reaction times and temperatures, much the same as there is leeway in the reaction vessels, type of agitation, etc., used. The treated cements then were quenched by injection with 1 ml of i-PrOH, treated with an antioxidant (3 ml of a mixture containing 1.6 wt% DBPC in hexane), coagulated in i-PrOH, air-dried at room temperature, then drum-dried. Suitable characterizations were performed. Characterizations are summarized in Table IX. Table IX also contains data for polymers prepared with n-butyllithium in the same way, in the absence of DDMI or THF. These were prepared as a comparison, to show the type of hysteresis behavior obtained in the absence of the initiator compositions of this invention. The relative hysteresis behavior is typical of that of nonfunctional polymers.

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Polymerization of Butadiene and Styrene, and End-linking with  $SnCl_4$ :

[0106] The above procedure was followed exactly, except that after 1.5 hour of polymerization at 50°C, the polymerization mixture was treated with 0.8 equivalent of  $SnCl_4$  per equivalent of Li charged. The products were worked up in the same manner as above, and the characterizations are also summarized in Table IX.

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## EVALUATION OF COMPOUNDED PROPERTIES

[0107] The product polymers were compounded and tested as indicated in the test recipe shown in Table I and cured 20 minutes at 165°C. Results of physical tests are summarized in Table X. In addition, the carbon-bound rubber content of the uncured, final compounded stocks of Examples 20 and 21 were 33 percent and 49 percent, respectively. This indicates an enhanced interaction between the polymer and carbon black in these cases, compared to unmodified rubber, which typically exhibits less than 23 percent carbon-bound rubber, and butyllithium-initiated, Sn-coupled rubber, which typically exhibits less than 35 percent carbon-bound rubber. The results of this test provided good evidence for reduced hysteresis in this polymer. The Dynastat  $\tan\delta$  (50°C) = 0.091-0.094 is about 50 percent below the value expected for an unmodified polymer of this microstructure and molecular weight, such as would be prepared using a typical alkylolithium initiator.

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TABLE IX  
CHARACTERIZATIONS OF POLYMERS FROM  $C_{12}H_{24}NLi \bullet 2THF$  INITIATORS

Example No.	Conditions	$T_g, ^\circ C$	%Sty	%1,2	Mw/Mn	$M_w/M_n$	%Coupl (6% HMW)
20	$C_{12}H_{24}NLi \bullet 2THF$ 50°C	-31.4	20.9	56.2	26.2	127724	1.25
21	$C_{12}H_{24}NLi \bullet 2THF$ 50°C - $SnCl_4$ -coupled	-34.4	21.0	53.7	86.1	215628	1.71
22	n-BuLi only, 50°C	-39.9	20.8	49.1	5.8	89631	1.17
23	n-BuLi only, 50°C $SnCl_4$ -coupled	-38.2	20.6	50.2	65.9	217335	1.51
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TABLE X  
COMPOUNDED EVALUATIONS OF POLYMERS PREPARED USING  $C_{12}H_{24}NLi \bullet 2THF$  INITIATOR

Example No.	Tensile Strength, MPa (psi)	% Elong. at break	MI/4-Cpd	Dispersion Index, %	% Bound Rubber	Dynastat, 1Hz, tan $\delta$ , 50°C
20	22.8 (3306)	441	74	91	33.0	0.091
21	25.3 (3673)	426	104	92	48.9	0.094
22	16.4 (2375)	427	30	96	9.2	0.186
23	26.9 (3024)	449	66	97	12.6	0.120

**Experiment No. 10**

**PREPARATION OF POLYMER FROM N-LITHIO(3,3,5-TRIMETHYL) HEXAHYDROAZEPINE INITIATOR**

5 [0108] Elastomers containing head-bound (3,3,5-trimethyl) hexahydroazepine (THMI) were prepared using N-lithio (3,3,5-trimethyl) hexahydroazepine initiator. Samples with and without end-linking with  $\text{SnCl}_4$  were prepared from the same living polymer in a manner similar to that described in the examples above. Characterizations and evaluations of the dynamic mechanical properties are summarized in TABLE XI below.

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TABLE XI  
CURED PROPERTIES OF SBR INITIATED WITH N-LITHIO (3,5-TRIMETHYL HEXAHYDROAZEPINE (LTHMI) INITIATOR  
(TEST RECIPE OF TABLE III)

Polymer No.	Feature	DSC, Tg, °C	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	Raw MLI/4	Dynastat, 1Hz, 50°C, tan δ	Wt% Bound Rubber
-	Sn-coupled control	-38	-	-	75	0.103	33.6
24	LTHMI-SBR-H	-38.7	102937	1.07	18.6	0.103	32.0
25	(LTHMI-SBR) <sub>4</sub> Sn	-38.7	191054	1.68	81.0	0.083	44.9

[0109] The data of TABLE XI show that the polymer of Example 24, initiated with the N-Li salt of the substituted cyclic

amine, had the same level of hysteresis and about the same amount of bound rubber as a low-hysteresis control polymer that had been end-linked with  $\text{SnCl}_4$ . The polymer of Example 25 that combined initiation by the substituted cyclic amine and end-linking with  $\text{SnCl}_4$  had a level of hysteresis about 20 percent lower than the control polymer with end-linking only. Furthermore, the levels of bound rubber that were measured for both of these N-Li amide-initiated examples indicated that there is a strong interaction between the polymers and the carbon black of the compounding recipe, especially in the polymer that combined amino-initiation and end-linking by Sn.

### Experiment No. 11

[0110] A tire that was prepared with treadstock containing an elastomer as described in this invention exhibited a reduced level of rolling loss, compared to an identical tire prepared with a treadstock containing a conventional elastomer.

[0111] A preferred method of preparing the initiators according to the invention, will now be described. A vessel, such as a small bottle containing a Teflon or glass-clad magnetic stirring bar, is dried, sealed, and purged with nitrogen.

The following is added by syringe while stirring:

1. 30 mmol anhydrous 2° amine in hydrocarbon solvent, and
2. 60 mmol anhydrous polar solubilizer in hydrocarbon solvent.

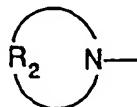
3. 30.1 mmol of alkyl lithium in hydrocarbon solvent is added by syringe at once, with stirring, while taking precaution for back-pressure (the larger ring amides may tend to precipitate if the alkyl lithium is added too rapidly).

[0112] The solution will heat and develop pressure immediately, but will soon begin to cool back down. When larger amounts of reagent are prepared, e.g. 250-300 mmol in large bottles or 0.5-1.5 mol in reactors, best results are obtained when chilled or cold water cooling is used to keep the peak temperature at about 38°C or below. The normal procedure has been to allow the mixture to stir overnight at room temperature before using. However, the reaction is essentially complete within minutes. The mixture should be clear, straw-yellow, without significant precipitation. Light-to-moderate haziness or cloudiness does not appear to affect activity. Anhydrous conditions are required. (SOL)/hydrocarbon solvent solutions with less than 30 ppm of water give best results. Initiator reagents can be stored under positive nitrogen pressures for periods of up to several weeks at room temperature (25-27°C). N-Lithio pyrrolidine-2THF solutions prepared and stored in this manner at about 0.5M - 1.5M in hexanes are stable for periods of about three to four weeks, and are effective initiators for diene and/or vinylaromatic (co)polymerizations, giving polymers with excellent properties. N-Lithio perhydroazepine-2THF solutions prepared and stored in this manner at about 0.3M - 0.9M in hexanes are stable for at least several days, and can also be used with good results in polymerizations.

[0113] It should now be clear from the foregoing examples and specification disclosure, that initiators according to the present invention are useful for the anionic polymerization of diene monomers. Reproducible polymerization of such polymers within a relatively narrow molecular weight range is achieved, and the resulting polymers also exhibit good preservation of live C-Li ends, when compared to the non-solubilized initiators heretofore known in the art.

### Claims

1. A functionalized polymer comprising:  
a polymer chain carrying at least one functional group selected from the group consisting of cyclic amine radicals having the general formula



55 where  $R_2$  is selected from the group consisting of a substituted alkylene group having from 8 to 16 methylene groups.

2. A functionalized polymer as in claim 1, wherein said polymer chain comprises at least one monomer selected from the group consisting of conjugated dienes having from 4 to 12 carbon atoms, monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes.

3. A functionalized polymer as in claim 1, wherein said functional group is selected from the group consisting of radicals of azacyclotridecane; azacycloheptadecane; 1-azacycloheptadec-9-ene; and, 1-azacycloheptadec-8-ene.

5 4. A functionalized polymer as in claim 3, wherein said functional group is bicyclic.

5. A functionalized polymer as in claim 4, wherein said bicyclic functional group is selected from the group consisting of perhydroisoquinoline, perhydroindole and 1,3,3-trimethyl-6-azabicyclo [3.2.1] octane.

10 6. A functionalized polymer as in claim 1, wherein said substituted alkylene is a mono- to octa-substituted alkylene.

7. A functionalized polymer as in claim 6, wherein the substituent of said substituted alkylene is linear or branched and has from 1 to 12 carbon atoms.

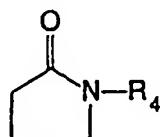
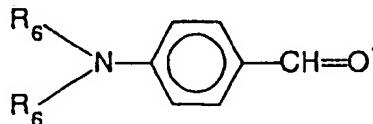
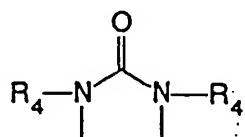
15 8. A functionalized polymer as in claim 7, wherein said substituent is selected from the group consisting of alkyls, cycloalkyls, bicycloalkyls, aryls, and aralkyls.

9. A functionalized polymer, as set forth in claim 1, prepared by the steps of forming a solution of one or more anionically polymerizable monomers in an alkane solvent; and, polymerizing said monomers in the presence of a polymerization initiator containing said functional group.

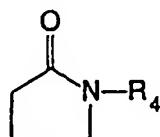
20 10. A functionalized polymer, as set forth in claim 9, wherein the process for its preparation comprises the further step of reacting said polymer with a second functional group selected and derived from the group consisting of terminating agents, coupling agents and linking agents, such that the resulting polymer is multifunctional.

25 11. A functionalized polymer, as set forth in claim 10, wherein said terminating agent, coupling and linking agents are selected from the group consisting of carbon dioxide; N,N,N',N'-tetraalkyldiaminobenzophenones; N,N-dialkylaminobenzaldehydes; 1,3-dialkylimidazolidinones; 1-alkyl substituted pyrrolidinones; 1-aryl substituted pyrrolidinones; dialkyl- and dicycloalkyl-carbodiimides having from 5 to 20 carbon atoms;  $(R_3)_aZX_b$ ;

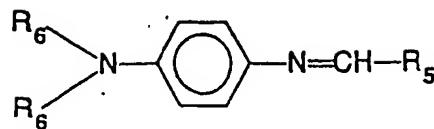
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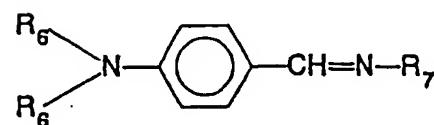
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20 where Z is tin or silicon; R<sub>3</sub> is selected from the group consisting of alkyls having from 1 to 20 carbon atoms, cycloalkyls having from 3 to 20 carbon atoms, aryls having from 6 to 20 carbon atoms and aralkyls having from 7 to 20 carbon atoms; X is chlorine or bromine; a is from 0 to 3 and b is from about 1 to 4 where a + b = 4; each R<sub>4</sub> is the same or different and is selected from the group consisting of alkyls, cycloalkyls and aryls, having from 1 to 12 carbon atoms; R<sub>5</sub> is selected from the group consisting of t-alkyls, phenyls, alkylphenyls and N,N-dialkylaminophenyls, having from 4 to 20 carbon atoms; each R<sub>6</sub> is the same or different, and is selected from the group consisting of alkyls and cycloalkyls having from 1 to 12 carbon atoms; and, R<sub>7</sub> is selected from the group consisting of alkyls, phenyls, alkylphenyls and N,N-dialkylaminophenyls having from 1 to 20 carbon atoms.

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12. A vulcanizable elastomeric compound having reduced hysteresis properties formed from a functionalized polymer as in claim 1 and from 5 to 80 parts by weight of carbon black, per 100 parts of said functionalized polymer.

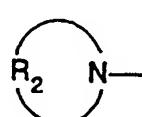
30 13. A tire having decreased rolling resistance and having at least one structural element selected from the group consisting of treads, subtreads, black sidewalls, body ply skims and bead fillers, wherein said structural element results from a vulcanizable elastomeric compound as set forth in claim 12.

35 14. A vulcanizable rubber composition comprising:

a polymer carrying at least one functional group A, wherein A is derived from the reaction product of an organolithium compound and an amine; and also carrying at least one tin-carbon bond derived from a terminating, coupling or linking agent (R<sub>3</sub>)<sub>a</sub>ZX<sub>b</sub>, where Z is tin or silicon; R<sub>3</sub> is selected from the group consisting of alkyls having from 1 to 20 carbon atoms, cycloalkyls having from 3 to 20 carbon atoms, aryls having from 6 to 20 carbon atoms and aralkyls having from 7 to 20 carbon atoms; X is chlorine or bromine; and, a is from 0 to 3 and b is from 1 to 4 where a + b = 4.

40 15. A vulcanizable rubber composition, as set forth in claim 14, where Z is tin.

45 16. A vulcanizable rubber composition, as set forth in claim 14, wherein A is selected from the group consisting of cyclic amine radicals having the general formula



55 where R<sub>2</sub> is selected from the group consisting of a substituted alkylene group having from 8 to 16 methylene groups.

17. A vulcanizable rubber composition as in claim 16, wherein said polymer comprises at least one monomer selected from the group consisting of conjugated dienes having from 4 to 12 carbon atoms, monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes.

5 18. A vulcanizable rubber composition as in claim 16, wherein said functional group A is selected from the group consisting of radicals of  
azacyclotridecane; azacycloheptadecane; 1-azacycloheptadec-9-ene; and, 1-azacycloheptadec-8-ene.

10 19. A vulcanizable rubber composition as in claim 18, wherein said functional group is bicyclic.

20 20. A vulcanizable rubber composition as in claim 19, wherein said bicyclic functional group is selected from the group consisting of perhydroisoquinoline, perhydroindole and 1,3,3-trimethyl-6-azabicyclo [3.2.1] octane.

21. A vulcanizable rubber composition as in claim 16, wherein said substituted alkylene is a mono- to octa-substituted alkylene.

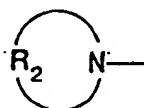
22. A vulcanizable rubber composition as in claim 21, wherein the substituent of said substituted alkylene is linear or branched and has from 1 to 12 carbon atoms.

23. A vulcanizable rubber composition as in claim 22, wherein said substituent is selected from the group consisting of alkyls, cycloalkyls, bicycloalkyls, aryls, and aralkyls.

24. A tire formed from the vulcanizable rubber composition of claim 14 and from 5 to 80 parts by weight of carbon black, per 100 parts of said polymer.

25 25. A tire, as set forth in claim 24, wherein A is selected from the group consisting of cyclic amine radicals having the general formula

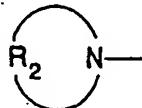
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35 where  $R_2$  is selected from the group consisting of a substituted alkylene group having from 8 to 16 methylene groups.

26. A functionalized polymer comprising:  
40 a polymer chain having the general formula  $AYLi$ ; wherein A is a functional group selected from the group consisting of cyclic amine radicals having the general formula

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50 where  $R_2$  is selected from the group consisting of a substituted alkylene group having from 8 to 16 methylene groups; and wherein Y is a divalent polymer radical selected from the group consisting of diene homopolymer radicals, monovinyl aromatic polymer radicals, diene/monovinyl aromatic random copolymer and block copolymer radicals.

27. A functionalized polymer as in claim 26, wherein said functional group A is selected from the group consisting of radicals of azacyclotridecane; azacycloheptadecane; 1-azacycloheptadec-9-ene; and, 1-azacycloheptadec-8-ene.

28. A functionalized polymer as in claim 27, wherein said functional group A is bicyclic.

29. A functionalized polymer as in claim 28, wherein said bicyclic functional group is selected from the group consisting of perhydroisoquinoline, perhydroindole and 1,3,3-trimethyl-6-azabicyclo [3.2.1] octane.

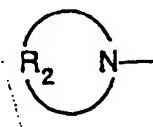
30. A functionalized polymer as in claim 26, wherein said substituted alkylene is a mono- to octa-substituted alkylene.

5 31. A functionalized polymer as in claim 30, wherein the substituent of said substituted alkylene is linear or branched and has from 1 to 12 carbon atoms.

10 32. A functionalized polymer as in claim 31, wherein said substituent is selected from the group consisting of alkyls, cycloalkyls, bicycloalkyls, aryls, and aralkyls.

#### Patentansprüche

15 1. Funktionalisiertes Polymer, umfassend:  
eine Polymerkette, die mindestens eine funktionelle Gruppe trägt, welche aus der Gruppe, bestehend aus cyclischen Amingruppierungen der folgenden allgemeinen Formel ausgewählt ist:



25 25. worin  $R_2$  aus der Gruppe, bestehend aus einer substituierten Alkylengruppe mit 8 bis 16 Methylengruppen, ausgewählt ist.

30 2. Funktionalisiertes Polymer nach Anspruch 1, wobei die Polymerkette mindestens ein Monomer, ausgewählt aus der Gruppe, bestehend aus konjugierten Dienen mit 4 bis 12 Kohlenstoffatomen, aromatischen Monovinyl-Monomeren mit 8 bis 18 Kohlenstoffatomen und Trienen, umfasst.

35 3. Funktionalisiertes Polymer nach Anspruch 1, wobei die funktionelle Gruppe aus der Gruppe, bestehend aus der Azacyclotridecan-, Azacycloheptadecan-, 1-Azacycloheptadec-9-en- und 1-Azacycloheptadec-8-en-Gruppierung ausgewählt ist.

40 4. Funktionalisiertes Polymer nach Anspruch 3, wobei die funktionelle Gruppe bicyclisch ist.

5. Funktionalisiertes Polymer nach Anspruch 4, wobei die bicyclische funktionelle Gruppe aus der Gruppe, bestehend aus Perhydroisochinolin, Perhydroindol und 1,3,3-Trimethyl-6-azabicyclo[3.2.1]octan ausgewählt ist.

45 6. Funktionalisiertes Polymer nach Anspruch 1, wobei das substituierte Alkylen ein mono- bis octa-substituiertes Alkylen ist.

7. Funktionalisiertes Polymer nach Anspruch 6, wobei der Substituent des substituierten Alkylens linear oder verzweigt ist und 1 bis 12 Kohlenstoffatome hat.

50 8. Funktionalisiertes Polymer nach Anspruch 7, wobei der Substituent aus der Gruppe, bestehend aus Alkyl, Cycloalkyl, Bicycloalkyl, Aryl und Aralkyl, ausgewählt ist.

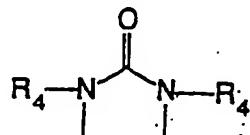
9. Funktionalisiertes Polymer nach Anspruch 1, das durch die Schritte Bilden einer Lösung eines oder mehrerer anionisch polymerisierbarer Monomeren in einem Alkan-Lösungsmittel und Polymerisieren dieser Monomeren in Gegenwart eines Polymerisationsinitiators, der die funktionelle Gruppe enthält, hergestellt ist.

55 10. Funktionalisiertes Polymer nach Anspruch 9, wobei das Verfahren zu seiner Herstellung den weiteren Schritt des Umsetzens des Polymeren mit einer zweiten funktionellen Gruppe, ausgewählt aus und abgeleitet von der Gruppe, bestehend aus Terminationsmitteln, Kupplungsmitteln und Verbindungsmitteln, umfasst, so dass das resultierende Polymer multifunktionell ist.

11. Funktionalisiertes Polymer nach Anspruch 10, wobei das Terminationsmittel, das Kupplungsmittel und das Verbindungsmittel aus der Gruppe, bestehend aus Kohlendioxid; N,N,N',N'-Tetraalkyldiaminobenzophenonen; N,N-Dialkylaminobenzaldehyden; 1,3-Dialkylimidazolidinonen; 1-Alkyl-substituierten Pyrrolidinonen; 1-Aryl-substituierten Pyrrolidinonen; Dialkyl- und Dicycloalkyl-Carbodiimiden, die 5 bis 20 Kohlenstoffatome haben;  $(R_3)_aZX_b$ ;

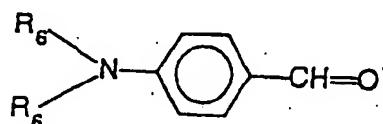
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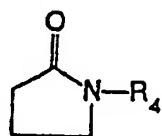


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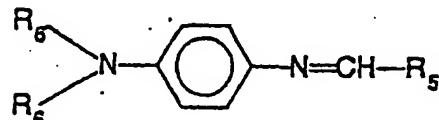


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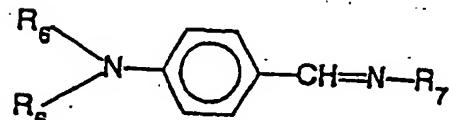
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und

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ausgewählt sind, worin Z für Zinn oder Silicium steht;  $R_3$  aus der Gruppe, bestehend aus Alkyl mit 1 bis 20 Kohlenstoffatomen, Cycloalkyl mit 3 bis 20 Kohlenstoffatomen, Aryl mit 6 bis 20 Kohlenstoffatomen und Aralkyl mit 7 bis 20 Kohlenstoffatomen ausgewählt ist; X Chlor oder Brom ist; a 0 bis 3 ist und b etwa 1 bis 4 ist, wobei  $a + b = 4$ ; die Reste  $R_4$  jeweils gleich oder unterschiedlich sind und aus der Gruppe, bestehend aus Alkyl, Cycloalkyl und Aryl mit 1 bis 12 Kohlenstoffatomen, ausgewählt sind;  $R_5$  aus der Gruppe, bestehend aus t-Alkyl, Phenyl, Alkylphenyl und N,N-Dialkylaminophenyl mit 4 bis 20 Kohlenstoffatomen ausgewählt ist; die Reste  $R_6$  jeweils gleich oder unterschiedlich sind und aus der Gruppe, bestehend aus Alkyl und Cycloalkyl mit 1 bis 12 Kohlenstoffatomen, ausgewählt sind und  $R_7$  aus der Gruppe, bestehend aus Alkyl, Phenyl, Alkylphenyl und N,N-Dialkylaminophenyl mit 1 bis 20 Kohlenstoffatomen, ausgewählt ist.

12. Vulkanisierbare elastomere Verbindung mit reduzierten Hystereseeigenschaften, die aus einem funktionalisierten

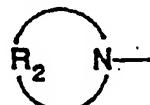
Polymer nach Anspruch 1 und 5 bis 80 Gew.-Teilen Ruß pro 100 Teile des funktionalisierten Polymeren gebildet wird.

5      13. Reifen mit verringertem Rollwiderstand und mit mindestens einem Strukturelement, ausgewählt aus der Gruppe, bestehend aus Laufflächen, Unterprotektoren, schwarzen Seitenwänden, Körperlagenskins und Wulstfüllmaterialien, wobei mindestens ein Strukturelement aus einer vulkanisierbaren elastomeren Verbindung nach Anspruch 12 resultiert.

10     14. Vulkanisierbare Kautschukzusammensetzung, umfassend:  
ein Polymer, das mindestens eine funktionelle Gruppe A trägt, worin A aus dem Reaktionsprodukt einer Organo-lithiumverbindung und einem Amin stammt; und das auch mindestens eine Zinn-Kohlenstoff-Bindung trägt, die von einem Terminations-, Kupplungs- oder Verbindungsmittel  $(R_3)_aZX_b$ , worin Z Zinn oder Silicium ist;  $R_3$  aus der Gruppe, bestehend aus Alkyl mit 1 bis 20 Kohlenstoffatomen, Cycloalkyl mit 3 bis 20 Kohlenstoffatomen, Aryl mit 6 bis 20 Kohlenstoffatomen und Aralkyl mit 7 bis 20 Kohlenstoffatomen, ausgewählt ist; X Chlor oder Brom ist; und a 0 bis 3 ist und b 1 bis 4 ist, wobei  $a + b = 4$ , stammt, trägt.

15     15. Vulkanisierbare Kautschukzusammensetzung nach Anspruch 14, wobei Z Zinn ist.

20     16. Vulkanisierbare Kautschukzusammensetzung nach Anspruch 14, wobei A aus der Gruppe, bestehend aus cyclischen Amingruppierungen der folgenden allgemeinen Formel ausgewählt ist:



worin  $R_2$  aus der Gruppe, bestehend aus einer substituierten Alkylengruppe mit 8 bis 16 Methylengruppen, ausgewählt ist.

30     17. Vulkanisierbare Kautschukzusammensetzung nach Anspruch 16, wobei das Polymer mindestens ein Monomer, ausgewählt aus der Gruppe, bestehend aus konjugierten Dienen mit 4 bis 12 Kohlenstoffatomen, aromatischen Monovinyl-Monomeren mit 8 bis 18 Kohlenstoffatomen und Trienen, umfasst.

35     18. Vulkanisierbare Kautschukzusammensetzung nach Anspruch 16, wobei die funktionelle Gruppe A aus der Gruppe, bestehend aus der Azacyclotridecan-, Azacycloheptadecan-, 1-Azacycloheptadec-9-en- und 1-Azacycloheptadec-8-en-Gruppierung, ausgewählt ist.

40     19. Vulkanisierbare Kautschukzusammensetzung nach Anspruch 18, wobei die funktionelle Gruppe bicyclisch ist.

45     20. Vulkanisierbare Kautschukzusammensetzung nach Anspruch 19, wobei die bicyclische funktionelle Gruppe aus der Gruppe, bestehend aus Perhydroisochinolin, Perhydroindol und 1,3,3-Trimethyl-6-azabicyclo[3.2.1]octan, ausgewählt ist.

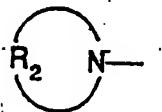
50     21. Vulkanisierbare Kautschukzusammensetzung nach Anspruch 16, wobei das substituierte Alkylen ein mono- bis octa-substituiertes Alkylen ist.

22. Vulkanisierbare Kautschukzusammensetzung nach Anspruch 21, wobei der Substituent des substituierten Alkylen linear oder verzweigt ist und 1 bis 12 Kohlenstoffatome hat.

55     23. Vulkanisierbare Kautschukzusammensetzung nach Anspruch 22, wobei der Substituent aus der Gruppe, bestehend aus Alkyl, Cycloalkyl, Bicycloalkyl, Aryl und Aralkyl, ausgewählt ist.

24. Reifen, der aus der vulkanisierbaren Kautschukzusammensetzung nach Anspruch 14 und 5 bis 80 Gew.-Teilen Ruß pro 100 Teile des Polymeren gebildet ist.

25. Reifen nach Anspruch 24, wobei A aus der Gruppe, bestehend aus cyclischen Amingruppierungen der folgenden allgemeinen Formel ausgewählt ist:



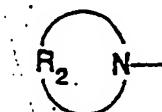
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wobei  $R_2$  aus der Gruppe, bestehend aus einer substituierten Alkylengruppe mit 8 bis 16 Methylengruppen, ausgewählt ist.

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26. Funktionalisiertes Polymer, umfassend:  
eine Polymerkette der allgemeinen Formel AYLi, worin A eine funktionelle Gruppe ist, welche aus der Gruppe, bestehend aus cyclischen Amingruppierungen der folgenden allgemeinen Formel, ausgewählt ist:

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worin  $R_2$  aus der Gruppe, bestehend aus einer substituierten Alkylengruppe mit 8 bis 16 Methylengruppen, ausgewählt ist; und worin Y eine zweiwertige Polymergruppierung, ausgewählt aus der Gruppe, bestehend aus Dienhomopolymer-Gruppierungen, aromatischen Monovinylpolymer-Gruppierungen, statistisches Dien/aromatisches Monovinyl-Copolymer-und -Blockcopolymer-Gruppierungen, ist.

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27. Funktionalisiertes Polymer nach Anspruch 26, wobei die funktionelle Gruppe A aus der Gruppe, bestehend aus Azacyclotridecan-, Azacycloheptadecan-, 1-Azacycloheptadec-9-en- und 1-Azacycloheptadec-8-en-Gruppierung ausgewählt ist.

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28. Funktionalisiertes Polymer nach Anspruch 27, wobei die funktionelle Gruppe A bicyclisch ist.

29. Funktionalisiertes Polymer nach Anspruch 28, wobei die bicyclische funktionelle Gruppe aus der Gruppe, bestehend aus Perhydroisochinolin, Perhydroindol und 1,3,3-Trimethyl-6-azabicyclo[3.2.1]octan ausgewählt ist.

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30. Funktionalisiertes Polymer nach Anspruch 26, wobei das substituierte Alkylen ein mono- bis octa-substituiertes Alkylen ist.

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31. Funktionalisiertes Polymer nach Anspruch 30, wobei der Substituent des substituierten Alkylens linear oder verzweigt ist und 1 bis 12 Kohlenstoffatome hat.

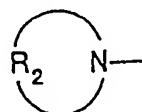
32. Funktionalisiertes Polymer nach Anspruch 31, wobei der Substituent aus der Gruppe, bestehend aus Alkyl, Cycloalkyl, Bicycloalkyl, Aryl und Aralkyl, ausgewählt ist.

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#### Revendications

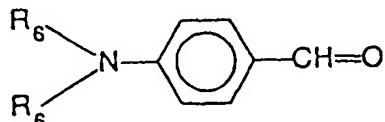
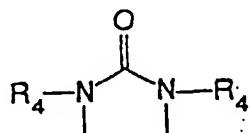
1. Polymère fonctionnalisé comprenant :  
une chaîne polymère portant au moins un groupe fonctionnel choisi dans le groupe consistant en des radicaux  
amine cycliques répondant à la formule générale

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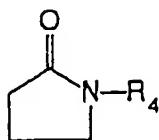


dans laquelle  $R_2$  est choisi dans le groupe consistant en groupes alkylène substitués ayant 8 à 16 groupes méthylène.

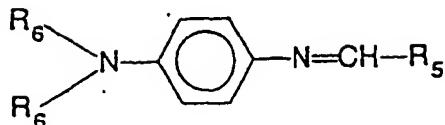
2. Polymère fonctionnalisé suivant la revendication 1, dans lequel la chaîne polymère comprend au moins un monomère choisi dans le groupe consistant en des diènes conjugués ayant 4 à 12 atomes de carbone, des monomères aromatiques monovinyliques ayant 8 à 18 atomes de carbone et des triènes.
3. Polymère fonctionnalisé suivant la revendication 1, dans lequel le groupe fonctionnel est choisi dans le groupe consistant en radicaux azacyclotridécane ; azacycloheptadécane ; 1-azacycloheptadéc-9-ène et 1-azacycloheptadéc-8-ène.
4. Polymère fonctionnalisé suivant la revendication 3, dans lequel le groupe fonctionnel est bicyclique.
5. Polymère fonctionnalisé suivant la revendication 4, dans lequel le groupe fonctionnel bicyclique est choisi dans le groupe consistant en la perhydro-isoquinoléine, le perhydro-indole et le 1,3,3-triméthyl-6-azabicyclo [3.2.1]octane.
6. Polymère fonctionnalisé suivant la revendication 1, dans lequel l'alkylène substitué est un alkylène mono- à octa-substitué.
7. Polymère fonctionnalisé suivant la revendication 6, dans lequel le substituant de l'alkylène substitué est linéaire ou ramifié et a 1 à 12 atomes de carbone.
8. Polymère fonctionnalisé suivant la revendication 7, dans lequel le substituant est choisi dans le groupe consistant en des substituants alkyle, cycloalkyle, bicycloalkyle, aryle et aralkyle.
9. Polymère fonctionnalisé suivant la revendication 1, préparé par les étapes consistant à former une solution d'un ou plusieurs monomères anioniquement polymérisables dans un solvant consistant en un alcane, et à polymériser lesdits monomères en présence d'un initiateur de polymérisation contenant ledit groupe fonctionnel.
10. Polymère fonctionnalisé répondant à la définition suivant la revendication 9, dont le procédé de préparation comprend l'étape supplémentaire consistant à faire réagir ledit polymère avec un second groupe fonctionnel choisi dans le, et dérivé du, groupe consistant en des agents de terminaison, des agents de couplage et des agents de liaison, de telle sorte que le polymère résultant soit multifonctionnel.
11. Polymère fonctionnalisé répondant à la définition suivant la revendication 10, dans lequel l'agent de terminaison, l'agent de couplage et l'agent de liaison sont choisis dans le groupe consistant en le dioxyde de carbone ; des  $N,N',N'$ -tétra-alkyldiaminobenzophénones ; des  $N,N$ -dialkylaminobenzaldéhydes ; des 1,3-dialkyl-imidazolidinones ; des pyrrolidinones à substituant 1-alkyle ; des pyrrolidinones à substituant 1-aryle ; des dialkyl- et dicycloalkylcarbodiimides ayant 5 à 20 atomes de carbone ;  $(R_3)_aZX_b$  ;



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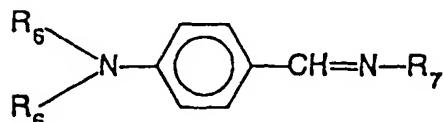


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25 dans lesquelles Z représente l'étain ou le silicium ; R<sub>3</sub> est choisi dans le groupe consistant en des radicaux alkyle ayant 1 à 20 atomes de carbone, des radicaux cycloalkyle ayant 3 à 20 atomes de carbone, des radicaux aryle ayant 6 à 20 atomes de carbone et des radicaux aralkyle ayant 7 à 20 atomes de carbone ; X représente le chlore ou le brome ; a a une valeur de 0 à 3 et b a une valeur d'environ 1 à 4, la somme a + b étant égale à 4 ; les radicaux R<sub>4</sub> sont identiques ou différents et sont choisis chacun dans le groupe consistant en des radicaux alkyle, cycloalkyle et aryle ayant 1 à 12 atomes de carbone ; R<sub>5</sub> est choisi dans le groupe consistant en des radicaux tertio-alkyle, phényle, alkylphényle et N,N-dialkylaminophényle, ayant 4 à 20 atomes de carbone ; les radicaux R<sub>6</sub> sont identiques ou différents et sont choisis chacun dans le groupe consistant en des radicaux alkyle et cycloalkyle ayant 1 à 12 atomes de carbone ; et R<sub>7</sub> est choisi dans le groupe consistant en des radicaux alkyle, phényle, alkylphényle et N,N-dialkylaminophényle ayant 1 à 20 atomes de carbone.

35 12. Composé élastomère vulcanisable présentant des propriétés d'hystérisis réduites, formé à partir d'un polymère fonctionnalisé suivant la revendication 1 et à partir d'une quantité de 5 à 80 parties en poids de noir de carbone, pour 100 parties dudit polymère fonctionnalisé.

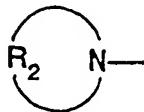
40 13. Bandage pneumatique présentant une résistance réduite au roulement et ayant au moins un élément structural choisi dans le groupe consistant en des bandes de roulement, des sous-couches de bandes de roulement, des flancs noirs, des skims en couche pour corps et des bandelettes support-talon, dans lequel ledit élément structural est obtenu à partir d'un composé élastomère vulcanisable répondant à la définition suivant la revendication 12.

45 14. Composition de caoutchouc vulcanisable comprenant :

un polymère portant au moins un groupe fonctionnel A, ledit groupe A étant dérivé du produit de réaction d'un composé organique de lithium et d'une amine ; et portant également au moins une liaison étain-carbone dérivée d'un agent de terminaison, de couplage ou de liaison (R<sub>3</sub>)<sub>a</sub>ZX<sub>b</sub>, dans lequel Z représente l'étain ou le silicium ; R<sub>3</sub> est choisi dans le groupe consistant en des radicaux alkyle ayant 1 à 20 atomes de carbone, des radicaux cycloalkyle ayant 3 à 20 atomes de carbone, des radicaux aryle ayant 6 à 20 atomes de carbone et des radicaux aralkyle ayant 7 à 20 atomes de carbone ; X représente le chlore ou le brome ; et a a une valeur de 0 à 3 et b a une valeur de 0 à 4, la somme a + b étant égale à 4.

55 15. Composition de caoutchouc vulcanisable répondant à la définition suivant la revendication 14, dans laquelle Z représente l'étain.

16. Composition de caoutchouc vulcanisable répondant à la définition suivant la revendication 14, dans laquelle A est choisi dans le groupe consistant en des radicaux amine cycliques répondant à la formule générale :



dans laquelle R<sub>2</sub> est choisi dans le groupe consistant en groupes alkylène substitués ayant 8 à 16 groupes méthylène.

10 17. Composition de caoutchouc vulcanisable suivant la revendication 16, dans laquelle le polymère comprend au moins un monomère choisi dans le groupe consistant en des diènes conjugués ayant 4 à 12 atomes de carbone, des monomères aromatiques monovinyliques ayant 8 à 18 atomes de carbone et des triènes.

15 18. Composition de caoutchouc vulcanisable suivant la revendication 16, dans laquelle le groupe fonctionnel A est choisi dans le groupe consistant en radicaux azacyclotridécane ; azacycloheptadécane ; 1-azacycloheptadéc-9-ène et 1-azacycloheptadéc-8-ène.

20 19. Composition de caoutchouc vulcanisable suivant la revendication 18, dans laquelle le groupe fonctionnel est bicyclique.

25 20. Composition de caoutchouc vulcanisable suivant la revendication 19, dans laquelle le groupe fonctionnel bicyclique est choisi dans le groupe consistant en la perhydro-isoquinoléine, le perhydro-indole et le 1,3,3-triméthyl-6-aza-bicyclo[3.2.1]octane.

21. Composition de caoutchouc vulcanisable suivant la revendication 16, dans laquelle l'alkylène substitué est un alkylène mono- à octa-substitué.

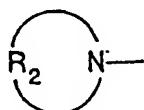
30 22. Composition de caoutchouc vulcanisable suivant la revendication 21, dans laquelle le substituant de l'alkylène substitué est linéaire ou ramifié et a 1 à 12 atomes de carbone.

23. Composition de caoutchouc vulcanisable suivant la revendication 22, dans laquelle le substituant est choisi dans le groupe consistant en des substituants alkyle, cycloalkyle, bicycloalkyle, aryle et aralkyle.

35 24. Bandage pneumatique formé à partir de la composition de caoutchouc vulcanisable suivant la revendication 14 et à partir d'une quantité de 5 à 80 parties en poids de noir de carbone, pour 100 parties dudit polymère.

25. Bandage pneumatique répondant à la définition suivant la revendication 24, dans lequel A est choisi dans le groupe consistant en des radicaux amine cycliques répondant à la formule générale

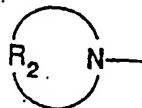
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dans laquelle R<sub>2</sub> est choisi dans le groupe consistant en groupes alkylène substitués ayant 8 à 16 groupes méthylène.

50 26. Polymère fonctionnalisé comprenant :  
une chaîne polymère répondant à la formule générale AYLI ; dans laquelle A représente un groupe fonctionnel choisi dans le groupe consistant en des radicaux amine cycliques répondant à la formule générale :

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10 dans laquelle  $R_2$  est choisi dans le groupe consistant en groupes alkylène substitués ayant 8 à 16 groupes méthylène ; et dans laquelle Y représente un radical polymère divalent choisi dans le groupe consistant en des radicaux homopolymères diéniques, des radicaux polymères aromatiques monovinyliques, des radicaux copolymères statistiques et copolymères séquencés diène/monomère aromatique monovinylique.

27. Polymère fonctionnalisé suivant la revendication 26, dans lequel le groupe fonctionnel A est choisi dans le groupe consistant en radicaux azacyclotridécane ; azacycloheptadécane ; 1-azacycloheptadéc-9-ène et 1-azacycloheptadéc-8-ène.

28. Polymère fonctionnalisé suivant la revendication 27, dans lequel le groupe fonctionnel A est bicyclique.

29. Polymère fonctionnalisé suivant la revendication 28, dans lequel le groupe fonctionnel bicyclique est choisi dans le groupe consistant en la perhydro-isoquinoléine, le perhydro-indole et le 1,3,3-triméthyl-6-azabicyclo[3.2.1]octane.

30. Polymère fonctionnalisé suivant la revendication 26, dans lequel l'alkylène substitué est un alkylène mono- à octa-substitué.

31. Polymère fonctionnalisé suivant la revendication 30, dans lequel le substituant de l'alkylène substitué est linéaire ou ramifié et a 1 à 12 atomes de carbone.

32. Polymère fonctionnalisé suivant la revendication 31, dans lequel le substituant est choisi dans le groupe consistant en des substituants alkyle, cycloalkyle, bicycloalkyle, aryle et aralkyle.

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